Art. V.—*A New Thermoelectric Phenomenon.*

(With Plate VII.)

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In text books on thermoelectricity it is usually stated that while an electromotive force may be caused by heating part of some metal, which either in its molecular condition, or in its shape, is not homogeneous or symmetrical, no electromotive force can be caused by heating a homogeneous piece. The experiments of Magnus in his paper on Thermoelectric Currents in *Pogg. Ann.*, 1851, are generally quoted as authority, but the experiments described below (performed in the Physical Laboratory of the University of Melbourne) seem to show that these statements require to be greatly modified. Magnus, using a very sensitive galvanometer, obtained a number of relative measurements of the electromotive force produced when similar wires at different temperatures were brought into contact, and when wires of the same material but different temper were heated in contact. But he got no effect from heating a single wire up to 100° C. But it appears that he had to take great precautions to prevent unequal heating or temper, or an e.m.f. was sure to appear. An important and interesting example of an electromotive force from one metal is described by Mr. F. T. Trouton *(Proc. Roy. Soc.*, 1886), where it is generated by moving a flame along a steel or iron wire slowly enough to make it red hot. The e.m.f., he says, is generated between the part which has cooled through the critical point and the part which is coming to it. This is of varying magnitude. In a recent report of a committee of the British Association to inquire into the phenomena connected with iron at a dull red heat it is stated that on bringing together a bright red iron wire and a cold one, an electromotive force of ·05 volt is generated. Both of these phenomena, but especially Trouton's, probably depend on the great change in the magnetic susceptibility of iron at a dull red heat.

It was in repeating Trouton's experiment that I found that great effects were produced by heating the iron wire steadily. This effect however was soon found to be very arbitrary and irregular, and steps were taken to obtain regular and systematic observations. A couple of yards of very hard iron wire were put in series with a sensitive galvanometer, the junctions of iron and copper being immersed in the same vessel of oil to insure their being at the same temperature and that no thermoelectric effects were generated in them. The iron was stretched into a loop and heated in various ways, such as warmed with the fingers, parts immersed in boiling water, in hot oil, in melted tin both bare and protected with asbestos, heated in a bunsen and in a blow-pipe flame, long portions heated in a tube furnace, and a small part was cooled by evaporating ether. In each case some effect was observed, though below 300° C. it was small, about the same order of magnitude as an ordinary thermal junction of silver and copper. Consistent results however were never obtained: if a certain effect were observed by heating part of the wire in a certain way, then on repeating the conditions a different effect would be observed, perhaps greater, perhaps less, and as likely as not of opposite sign. When kept heated steadily the effect was not constant. It increased, decreased, kept steady, changed sign, vanished and reappeared in the most arbitrary way imaginable, and showed no sign of becoming steadier even after being left alone for half-an-hour. Below a dull red heat these changes were slow, but fast enough to keep the galvanometer needle moving perceptibly, but above a red heat the changes were too fast for the needle to follow dead beat, and it was kept continually oscillating. These oscillations were sometimes small, perhaps ten per cent. of the total deflection, while at others the needle was jerked about so widely that one could not even form a mental estimate of the changes of electromotive force, much less make a note of them. I tried various samples of iron wire of different hardness and thickness, from ·2 mm. to a bar 1 cm. diameter. The effect was observed in each case, it being as a general rule more marked in the finer wires than the coarser. The highest effect I observed in iron was about ·002 volt. On passing the wires through tubes, glass or clay, and heating them, very little effect could be obtained.

After working at the iron for some days I treated a copper wire similarly to see if the effect existed in it too, but could not find a trace of it. The copper wire was a thick one, and this was before I noticed the effect greater in fine wire than coarse. I came to the conclusion that the effect was in some way connected with the magnetic property of iron, and for some time confined my attention to it. After a while, however, I tried a fine brass wire, and instantly found the effect marked, about ·0001 volt. As the wire was heated in the naked flame it soon fused. On twisting the ends together and heating the junction ·001 volt was indicated. Platinum wires of ·8 and ·4 mm. diameter gave very small effects, but a very fine wire of ·06 mm. diameter gave ·0001 volt. Copper wire 1·7 mm. gave no effect, as already stated. ·3 mm. gave ·00002 volt, and one of ·14 mm. ·0001 volt. These values were all obtained by heating the wires in a flame, but as all except the platinum fused almost instantly even in a candle flame I had to take steps to protect them. The most obvious plan was to pass them through glass tubes, but at a red heat there seemed to be chemical action between some of the metals and the glass, so the glass tubes were abandoned for clay tobacco pipe stems. Even the finest wires could be heated for some time in these without burning through or fusing.

Gold wire, when heated, presented some interesting peculiarities. The first tried was an alloy of gold and silver, 62 per cent. gold (fifteen carats). It was somewhat fine wire, ·26 mm. diameter. I found the effect well marked, though at first not so great as in iron, but more steady. The effect was not constant, but the changes took place very slowly, so that the galvanometer needle moved dead beat. Repeated heating and cooling the same part greatly increased the effect, this was not noticed in iron. Frequently on cooling the tube I noticed an extraordinary effect. On turning off the gas there were almost immediate, and apparently instantaneous, rises, sometimes of fifty per cent., sometimes as much as one hundred per cent., though only temporary; one of these sudden rises reached ·01 volt. While repeating the experiment the wire fused, and I had to take a fresh piece. On several occasions I found that by shifting the flame back and forward over an inch or two of the wire that there were points which gave a maximum effect, intermediate points giving little or none. By thus shifting the flame about I occasionally got very large effects, once reaching ·02 volt, at which it was steady for some time. This was by far the largest effect I had yet observed in any metal. I afterwards obtained two wires drawn from standard gold, 92 per cent. gold, 8 per cent. copper, these were about 1 mm. and ·5 mm. diameter. Neither gave any effect when heated up to melting point in a naked flame, and I could get no effect at all by heating the coarser one in a clay tube. On heating the finer in a clay tube moderate effects, *e.g.*, ·0001 volt, were observed. On attempting to draw the hot wire through the tube it parted. On pushing the broken end into the tube again there was an enormously high effect, but before the resistances could be altered it had fallen somewhat, and when the needle had become steady enough to indicate the amount, it was ·3 volt, though I think it must have been quite ·5, but ·3 was the highest I read, and that I can vouch for. On allowing the tube to cool it was found that the wire was stuck. The tube was cracked open, and it was seen that the gold had fused into a lump the thickness of the tube, and about 1 cm. in length. Another wire was heated, and after the flame had been shifted, about ·025 volt was reached, another shift giving ·13 volt. The effect was always much greater after the wire was fused and the ends pushed together. For the most part with gold the effect was temporary, none of those over ·1 volt lasting more than fifteen seconds, though on one occasion a steady ·18 volt was obtained. The effect was nearly always increased by disturbing the system in any way, such as shifting the flame or pulling the wire along the tube. When the junction of the thick and thin wires was heated the effect was much the same as with the thin wire by itself, but as a rule it was greater and more permanent, and with one exception, which was only for a few seconds, it was always in the same direction—the currents flowing from thin to thick. I alternately heated and cooled such a junction, and at last obtained a temporary effect of ·33 volt, which dropped quickly to ·3 and remained steady. After some time I shifted the flame in hopes of raising it, but it fell. On another occasion it increased steadily to ·29 volt and remained steady till disturbed.

In the early part of my work I used the most sensitive galvanometer obtainable—a low resistance, astatic instrument, with telescope and a scale at some distance. I soon found that there was no necessity for such a sensitive arrangement, as the needle was constantly going off the scale. It was also necessary for me to measure the resistance of the circuit each time it was altered, *i.e.*, each time a wire was fused or broken and had to be renewed. This was troublesome and took up a lot of time, and I soon found it more convenient to use a high resistance though less sensitive galvanometer, which I arranged to give direct readings as a volt meter and save the trouble of reducing the readings. The lamp and scale was at a distance of forty inches from the concave mirror on the needle which formed on the scale an image of a lens with a dark vertical hair-line immediately in front of the lamp, the lens serving to concentrate on the mirror a larger amount of light from the lamp than it would otherwise have received. The scale had 350 divisions on each side of zero. The galvanometer resistance was 7,400 ohms; in series with this I added 2,600 and another 90,000, which could be short circuited, so that neglecting the resistance of the wires under observation I could have a resistance of either 10,000 or 100,000 ohms. The galvanometer was also provided with three shunts $\frac{1}{9}$, $\frac{1}{99}$, and $\frac{1}{999}$ of its own resistance. Now, putting a Leclanche cell of 1·45 volts into circuit with the 100,000 ohms and the $\frac{1}{99}$ shunt I adjusted the height of the control magnet till the deflection was 145 scale divisions. With this arrangement the readings were always very approximately in decimals of a volt whatever shunt was used. Thus with 10,000 ohms and no shunt, 100 scale divisions indicated ·001 volt; with 100,000 ohms, ·01 volt; with same resistance and $\frac{1}{9}$ shunt, ·1 volt; $\frac{1}{99}$ shunt, 1 volt; and with $\frac{1}{999}$ shunt, 10 volts, so that by adjusting two plugs the one instrument would indicate ·00001 volt and measure 35 volts. I found this arrangement very satisfactory. For perfect accuracy the external resistance should have been slightly different for each shunt, but neglect of this caused an error of only two or three per cent., and I aimed at quickly getting the magnitudes of the effects involved rather than a very accurate measure of them. It may perhaps be convenient to those who are not familiar with the magnitude of the ordinary thermoelectric phenomenon to quote a few figures, so that the relative amounts of ordinary thermoelectric forces and those which I am describing may be readily compared.

The table shows the temperatures at which three different thermoelectric junctions will generate various electromotive forces, the cold junctions being at 0° C.

E.M.F.	·0001 volt.	·001 volt.	.01 volt.	·1 volt.	·3 volt.
Lead Copper	60°C	336	1310	4420	7760
Lead Bismuth ...	2	16	150	921	1870
Antimony Bismuth ...	1	9	85	522	1064

The above are based on Professor Tait's results.

Returning now to the phenomenon under consideration, I may say that, in this paper, I am not following altogether the order of my experiments, but am giving all experiments on one metal together, though I frequently left a metal and returned to it again.

In platinum there was apparently an anomalous result. Two unequally thick wires and a very fine one were stretched in series, the fine being between the other two. Heating the junction of the fine and coarsest gave ·0027 volt; while the fine and medium gave ·0007, *both in the same direction;* one would expect that in each case it would be from fine to coarse or *vice versâ.* It may however have been due to different amounts of impurity in the specimens. When the medium wire was heated by itself there was no perceptible result, the coarsest gave ·0001 volt and the fine gave various amounts up to ·0023 volt.

Fine brass wire heated in a tube behaves similarly to iron when heated in a flame, the effect being very unsteady. It is much less sensitive than gold to being disturbed; the highest effect I observed with brass was ·015 volt.

The behaviour of German silver was, in many respects, similar to gold. The effect was greatly increased by repeated heating and cooling, and the changes were generally slow and steady, though occasionally without any apparent cause the changes became great and abrupt, as much as with iron. Like gold too it showed distinct positions of maximum and minimum effects, they being even more marked than in the case of gold. Plate VII. shows the best example of this I ever obtained, but I could never again get one nearly so good. The time occupied in taking the observations from which it is drawn was about two hours. When the flame was shifted forward a centimetre, the needle crept slowly to the next position, there not being a single oscillation the whole time. For a long time I had been unable to obtain more than ·001 volt from German silver, but on one occasion I found two different parts of a wire, one of which gave ·0014, the other ·0016, giving the same values after several heatings. I then heated them simultaneously and got ·0031, which afterwards increased to ·0042, and after being heated and cooled several times increased to ·0047, the wire then fused. On another occasion, after heating a wire for some time, with little effect, I left the flame alone for a considerable time, and the electromotive force rose steadily to ·0045, and unsteadily to ·0052, and then fell as suddenly as if the wire had parted, but it had not, for on the oscillations of the needle dying out there was still a small deflection.

To examine lead I first of all dipped part of a lead wire into hot oil, but could get no effect. I afterwards melted some lead in the bowl of a pipe and heated the stem so as to make it run along and fill it up. The lead could thus be heated far above its melting point without running away and breaking circuit. On heating this tube the effect was apparent at once, and on irregular heating soon became considerable, ·001 volt. The tube was then heated systematically from end to end, and it was found that there was about an inch towards one end which always gave great results when heated, while at all other parts the effect was very small. After several heatings ·013 volt was observed at this critical point. Though the movements of the galvanometer needle were very slow and generally dead beat, yet, about this part, there were some peculiar effects. On one occasion, on applying the flame to this point, the galvanometer reading rose steadily to 110, decreased unsteadily to 10, and then swung unsteadily between 90 and 10 in such way as to indicate sudden and systematic rises and falls of electromotive force, though the flame was not disturbed and the temperature of the lead was constant, and there was nothing apparent which could have caused these changes. At another time the reading being 30, not very steady, I removed the flame, the reading fell steadily to 10 and then jerked to 60, after which it gradually decreased to zero. These jerks on the removal of the flame occurred so frequently as to make one of the characteristics of the phenomenon in the case of lead. Sometimes on heating the lead the readings rose gradually from zero, and at others there was no effect for some minutes when a sudden great deflection occurred. Another pipe stem was taken and a lead wire drawn down till it could be pushed along it, and on heating it I at last got ·2 volt. At the time this was by far the greatest effect yet observed. On one occasion after heating the tube in the usual way I removed the flame at a time when the reading was steady at zero. The e.m.f. rose quickly, but not suddenly, to ·07 volt, and then decreased. As a type of the general behaviour of lead I will describe the chief movements which took place in forty-five minutes, during which the flame was not disturbed. After a little preliminary heating the needle began to move and indicated ·02 volt, then reversed and rose gradually to ·17, but decreased to ·16, at which it remained steady for some time. It decreased further to ·1, but rose to ·185 and kept steady at ·18 ; decreased to ·05, rose to ·1, at which it kept for five minutes, then went on to ·15, and ·18, after which it fell and reversed to ·07, but soon came back to ·1, and on to ·205, fell to ·1, rose to ·15, fell to ·05, but came back to ·2, and again fell and reversed to –·05 for a few seconds only, after which it rose again to ·15 ; reversed again to –·08, and –·1, and back to ·205, remained steady at ·203 for half-a-minute. It fell again and reversed to –·02, rose to ·1, and again reversed to –·13. The gas was then turned off for the night. There were many smaller motions superposed on the larger ones, but were quite irregular. In spite of the occasional excursions to the negative side, the deflections were on the one side for the great bulk of the time, –*ve* and +*ve* are, of course, quite arbitrary. The motions were all dead beat except some of the negative deflections, which were so quick and so short that they set up oscillations in the needle. When the gas was lighted again next morning, the system not having been disturbed, there was no effect after five minutes. The flame was then shifted about, but no effect more than ·0005 volt could be got. I tried several other tubes with lead wires passed through them and found the behaviour much the same in each case, ·15 volt being observed frequently, and ·2 occasionally. It had nearly always been necessary to shift the flame and thus set up irregular heating before the effect could be observed in any considerable degree. To see if the effect could not be obtained from a perfectly symmetrically heated system, I took a fresh tube, and passing a wire along it applied a flame to the middle, prepared to watch it, if necessary, half-an-hour. There was no effect for a minute, the e.m.f. then became manifest and rose quickly to ·035 volt, and fell again to ·03. Then after rising and falling irregularly for a time it soon reached ·13 volt. Forty-five minutes after lighting the readings changed sign but did not get higher than ·05 on the other side. After an hour I began to heat it irregularly, but did not get more than ·15 volt. With lead a very slight cooling of the tube caused the effect to disappear. Merely cutting off the supply of air from the bunsen flame was always followed by a very great decrease, if not a complete disappearance, of the effect, although the luminous flame kept the tube at a moderate red heat. An estimation of the temperature reached inside the tube, made by means of a copper platinum junction with specimens in which I had not been able to observe this other effect, showed that with the bunsen flame 900° C. was reached, and with a blowpipe 1050°. I only used the blowpipe occasionally, generally using an ordinary bunsen flame.

Filling a tube with tin as the first had been filled with lead no effect higher than ·0001 volt was observed for half-an-hour either by steady or irregular heating. At last there was a large and sudden swing of the needle and on its coming to rest it indicated ·15 volt, remaining between ·12 and ·15 for several minutes. Various parts of the tube were heated, and as in the case of the first lead tube there was one point in particular which gave great effects. After leaving it for a couple of days and again applying the flame to this point ·3 volt was indicated almost at once, and for half-an-hour from ·28 to ·31 volt was maintained, only once did it fall to ·21 but instantly rose again. While at its height the gas was turned off. There was a steady and very slow fall, ·01 volt still remaining after ten minutes. The gas was lighted again and ·28 was soon indicated again.

Several other tubes were filled with tin and heated, and with one exception all gave from ·1 to ·2 volts, from the remaining one only infinitesimal results could be obtained. The changes of e.m.f. were much slower in tin than in lead, but it was very sensitive to the flame being shifted along the tube, a few millimetres of shift sometimes causing a great variation in the galvanometer reading. There were no abrupt changes as in the case of lead on removing or lowering the flame. A tin wire (alloyed with lead) when put through a tube and heated behaved similarly to tin and lead, ·16 volt was obtained from it.

I could not get a tube filled with zinc in the same way as I had filled others with lead and tin, but I managed to get one filled by exhausting it while the end was dipped into a crucible of melted zinc. The highest e.m.f. I observed with this was only ·00035, but that was partly, if not wholly, due to the hot junction of the zinc and copper, as the tube of zinc was very short. I afterwards got some zinc wire and passed it along a tube and heated it. There was no result at first, and the wire fused and broke circuit as the diameter of the wire was much less than the bore of the tube. When the ends were pushed in and contact renewed ·05 volt was indicated, but it quickly fell to ·004. On shifting the flame there were various smaller effects, but after cooling and heating several times ·2 volt was at length reached, the behaviour not being in any way characteristic. At a time when the e.m.f. was ·01 and falling slowly I turned off the gas. It fell somewhat faster, though still slowly, and after some minutes, when the tube was cool enough to be held in the fingers, ·006 volt was still indicated. The temperature of the zinc could not have been over 200°.

As already mentioned I had examined copper to see what effect could be obtained from it and had only reached ·0001 volt. After obtaining such high effects in other metals I returned again to copper, using the finest wire I could get, this was ·16 mm. diameter, and silvered, but the silver disappeared almost instantly on heating. After a little irregular heating, ·001 volt was reached, the changes being very slow, and oscillations of the needle being scarcely perceptible. After some time, however, there was a sudden swing indicating a change from ·0002 to –·001, then suddenly back to ·016, and steadily on to ·034, then a sudden great swing much higher still, but it fell before a reading could be taken. On cooling it fell steadily to zero. When heated again the effect rose steadily to ·25 volt, and for some time rested steadily between ·23 and ·25. Shifting the flame back and forward increased the effect to ·28, and it remained steady at ·27 for some time, and on shifting the flame along the whole tube I found two places about 2 mm. apart which gave maximum effects of + ·27 and – ·25 volt. The wire then parted. In repeating the experiment with other samples of the same wire I could never again get the great effects of the second part of the experiment, though ·001 was reached frequently enough. Several times on turning out the gas I noticed that the readings decreased very slowly, and once when the tube could be held comfortably in the fingers ·0002 volt was still indicated. I dipped part of the wire into hot oil at about 250° when ·0006 volt was given, while at 900° only ·001 had been given.

A tube was filled with antimony by exhaustion, and on heating it ·27 volt was given almost at once, but not for long. ·1 volt was reached again, but after a time I could get none. Another tube gave ·01 volt with the bunsen flame, and ·015 with the blowpipe. I made several other efforts to fill tubes with antimony, but failed, as the metal was not continuous through the tube.

With bismuth the highest effect observed was ·06 volt, but I did not keep at it very long.

Silver wire heated in a glass tube gave ·00007, which, when the flame was removed, rose to ·0007. When heated in a clay tube ·0008 was reached after several heatings and coolings. In another piece ·001 was reached after a time, but only temporarily. The effect was never steady, though more so than with iron. Another sample of very pure silver gave various effects up to ·0001.

Thallium gave various effects up to ·0005 volt, but I did not keep at it long as it attacked the clay, and I did not wish to lose it.

Magnesium was a difficult metal to examine. Heated in air it oxidises instantly, and heated in clay or glass it combines with the silicon and the resistance becomes infinite almost at once. In the clay tubes, however, I once got a reading of ·03, and a single swing indicating ·1 volt. I tried it by wrapping it in asbestos. The general effect was small at first, but there was generally a big swing when the magnesium parted, ·3 volt being once indicated. On another occasion, after igniting in the asbestos ·03 volt was indicated, but as the resistance was very great it was really much more.

With aluminium I could not get any great effect. When heated in a clay tube there was at once a deflection indicating ·0002 volt, but it soon decreased to about two-thirds of this, and after a few seconds to zero, and there was no further effect till the flame was shifted, when the same effect was repeated. Heating in a flame without the tube gave larger and more irregular effects, once up to ·0009, and another sudden heating gave a temporary ·003. With another specimen the highest effect was ·0001 volt.

In conclusion then, in contradiction to the commonly received statement, thermoelectric forces, in many cases of a high order of magnitude, have been observed by heating a homogeneous conductor. This been detected in twelve different metals and four alloys and may fairly be taken as a common property of all metals. The effect cannot be due to chemical change, because it is manifest in some cases at very low temperatures. It is not due to differences of thickness of the metal as mentioned by Clerk Maxwell. It is not due altogether to irregular or unsymmetrical heating, because it was observed several times when symmetrically heated. It is not altogether due to the action of the clay on the metals because it has been observed without the clay, though it must be remembered that the very high effects were all observed in clay tubes. The abruptness with which the effect occurs or increases at times when the temperature is rising steadily, or, strangest of all, falling, is one of the most extraordinary characteristics of the phenomenon; this frequently occurs with certain metals, particularly lead, never with others. The phenomenon is independent of the Thomson effect, for it is much more marked in lead in which the Thomson effect is zero, than in iron in which it is very high. The metals in which I observed the highest effects are not necessarily those in which the effect is really highest, for I examined some for weeks and others only for a few minutes. Most of the time was spent over iron, lead, and gold (ninety-two per cent.) The purest metal I used was silver, one of the specimens being absolutely pure, and with this the effect was very small. The effect however cannot be altogether due to impurity, for with alloys the effect was not more marked than with moderately pure metals.